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Form Approved
OMB No. 0704-0188

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1. REPORT DATE	2. REPORT TYPE Viewgraphs		3. DATES COVERED	
4. TITLE AND SUBTITLE Chiral Polymers for Optical Waveguides			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) W. N. Herman; G. A. Lindsay; D. Irvin; A. Guenthner; A. Chafin			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Air Warfare Center Aircraft Division 22347 Cedar Point Road, Unit #6 Patuxent River, Maryland 20670-1161			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT				
15. SUBJECT TERMS Polymers; Chiral; waveguides				
16. SECURITY CLASSIFICATION OF: a. REPORT		17. LIMITATION OF ABSTRACT b. ABSTRACT	18. NUMBER OF PAGES c. THIS PAGE Unclassified	19a. NAME OF RESPONSIBLE PERSON Dr. Warren Herman
				19b. TELEPHONE NUMBER (include area code) (301) 342-9114

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18

20010824 081



CHIRAL POLYMERS FOR OPTICAL WAVEGUIDES

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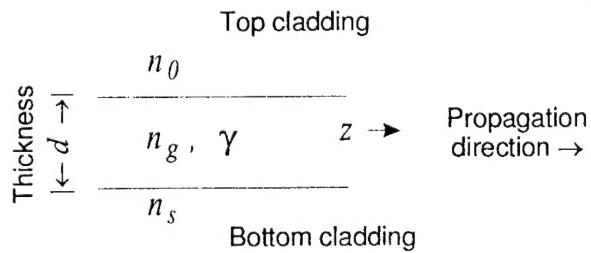
U.S. Navy, NAWCWD

Chemistry and Materials Division, China Lake, CA

26 August 2001



Potential Application for Chiral Polymers: Chiral Core Optical Waveguides



ISOTROPIC CHIRAL MEDIUM

**Constitutive Relations
(Drude-Born-Fedorov)**

$$\bar{D} = \epsilon(\bar{E} + \gamma \nabla \times \bar{E}) \quad \bar{B} = \mu(\bar{H} + \gamma \nabla \times \bar{H})$$

Bohren's Decomposition

$$\bar{E} = \frac{1}{2}(\bar{F}^+ + \bar{F}^-) \quad \bar{H} = \frac{1}{2i\sqrt{\frac{\epsilon}{\mu}}}(\bar{F}^+ - \bar{F}^-)$$

Wave Equation

$$\nabla^2 \bar{F}^\pm + (k_0 n_\pm)^2 \bar{F}^\pm = 0$$

**Eigenmodes in bulk
material circularly polarized**

$$\bar{F}^\pm = \bar{E}_0 e^{i(k_0 n_\pm z - \omega t)} (\hat{x} \pm i\hat{y})$$

**Refractive indices
for RH and LH
waves**

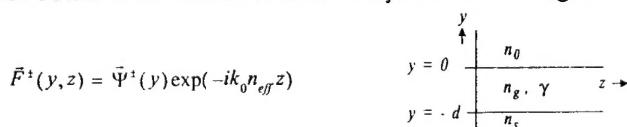
$$n_\pm = \frac{n_g}{1 \pm \delta} \quad \delta = k_0 n_g \gamma \quad n_g = \sqrt{\frac{\epsilon}{\epsilon_0}} \quad k_0 = \frac{2\pi}{\lambda}$$

Rotatory Power

$$\rho = \frac{\pi(n_- - n_+)}{\lambda} \approx k_0 n_g \delta$$

A. Lahtakia, V.K. Varadan, and V.V. Varadan, Time-Harmonic Electromagnetic Fields in Chiral Media, Lecture Notes in Physics Series 335 (Springer-Verlag, Berlin, 1989).
 I.V. Lindell, A.H. Silvola, S.A. Tretyakov, A.J. Viitanen, Electromagnetic Waves in Chiral and Bi-isotropic Media, (Artech House, Norwood, MA, 1994).

General Solution for Modes in Chiral Asymmetric Waveguide



Modal equations: (3 equations to be solved simultaneously for n_{eff} , g , h)

$$\begin{aligned} F^\pm(y, z) &= \bar{\Psi}^\pm(y) \exp(-ik_0 n_{eff} z) \\ u^\pm d &= \cot^{-1} \left(\sigma_0^\pm \frac{r_0 \pm g}{1 \pm g} \right) + \cot^{-1} \left(\sigma_i^\pm \frac{r_i \pm h}{1 \pm h} \right) + m^\pm \pi \\ h(g, n_{eff}) &= \frac{(Sr_0^+ - Sr_0^-) + (S_0^+ + S_0^-)g}{(Sr_0^+ + Sr_0^-) + (S_0^+ - S_0^-)g} \end{aligned}$$

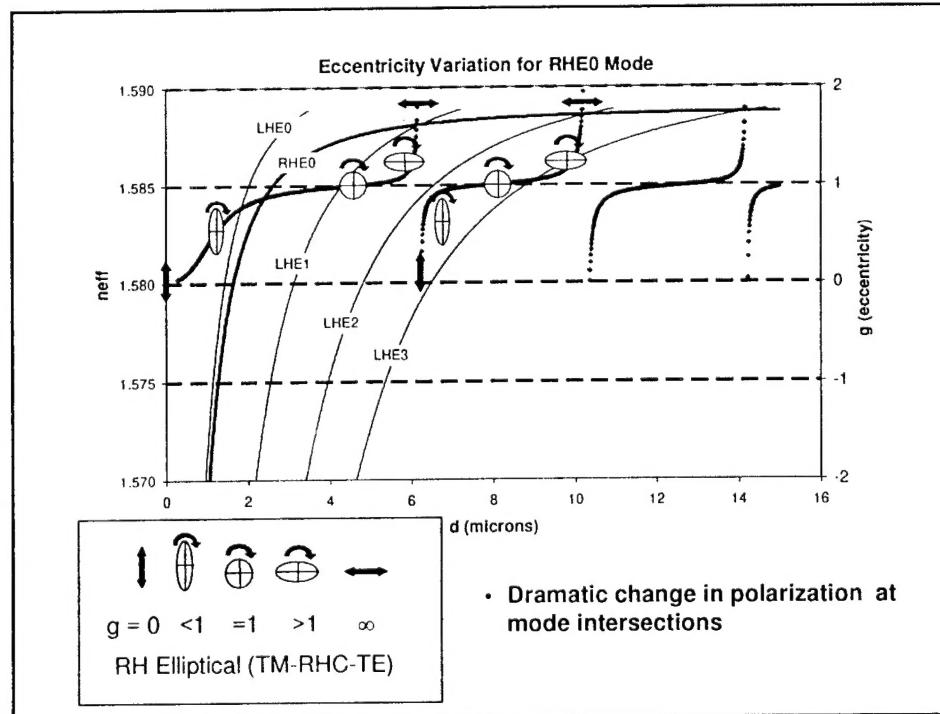
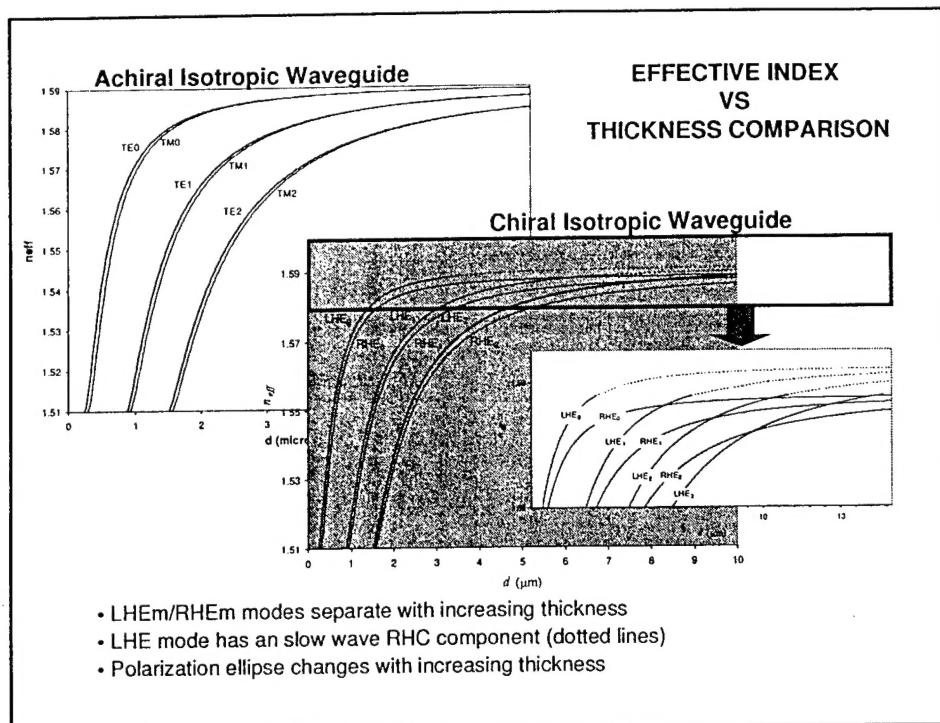
$$\begin{aligned} S_0^\pm &= \sigma_0^\pm \sin(u^\pm d) - \cos(u^\pm d) \\ Sr_0^\pm &= r_0 \sigma_0^\pm \sin(u^\pm d) - \cos(u^\pm d) \end{aligned}$$

$$\begin{aligned} \sigma_0^\pm &\equiv (1 \pm \delta) \frac{u^\pm}{v}, \quad \sigma_i^\pm \equiv (1 \pm \delta) \frac{u^\pm}{w}, \quad r_0 \equiv \frac{n_0^2}{n_g^2}, \quad r_i \equiv \frac{n_i^2}{n_g^2} \\ u^\pm &\equiv k_0 \sqrt{n_\pm^2 - n_{eff}^2}, \quad v \equiv k_0 \sqrt{n_{eff}^2 - n_0^2}, \quad w \equiv k_0 \sqrt{n_{eff}^2 - n_i^2} \end{aligned}$$

Parameters g , h determine eccentricity of polarization ellipse for transverse E-field:

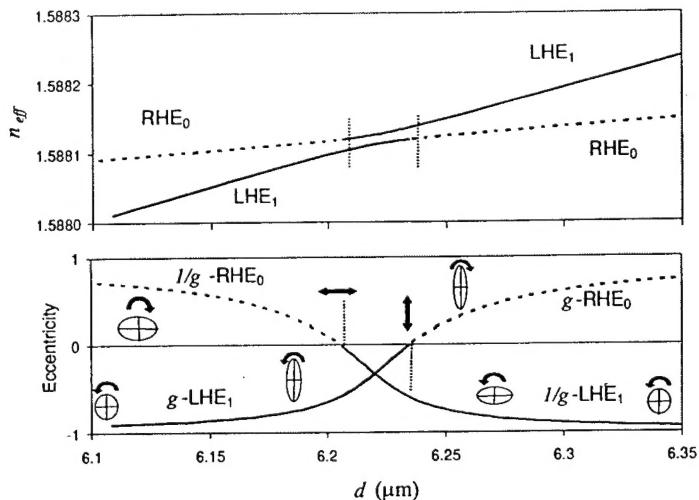
$$\left. \frac{E_x}{E_z} \right|_{z=0} = i \frac{n_{eff}}{n_g} \frac{1}{g} \quad \left. \frac{E_y}{E_z} \right|_{z=d} = i \frac{n_{eff}}{n_g} \frac{1}{h}$$

W. N. Herman, in press *J. Opt. Soc. Am. A*

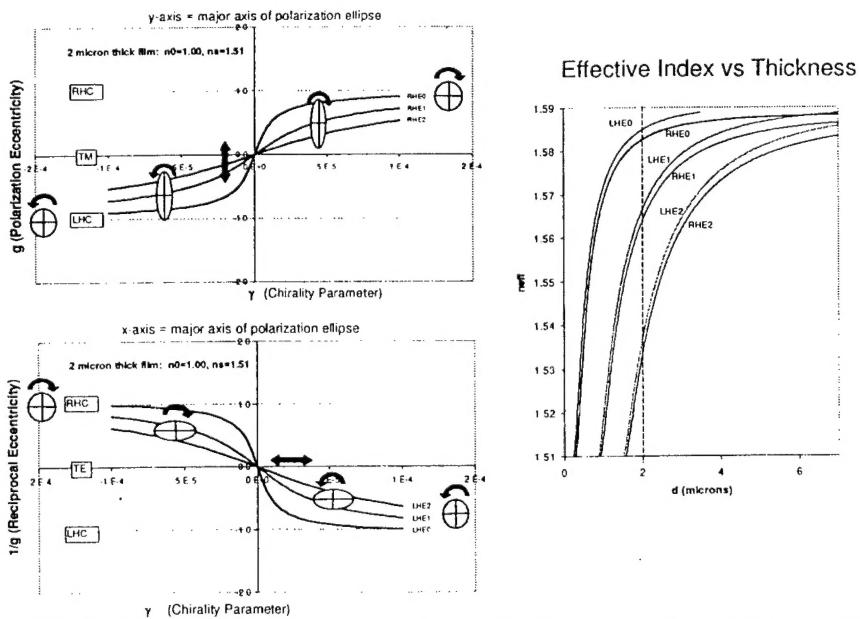


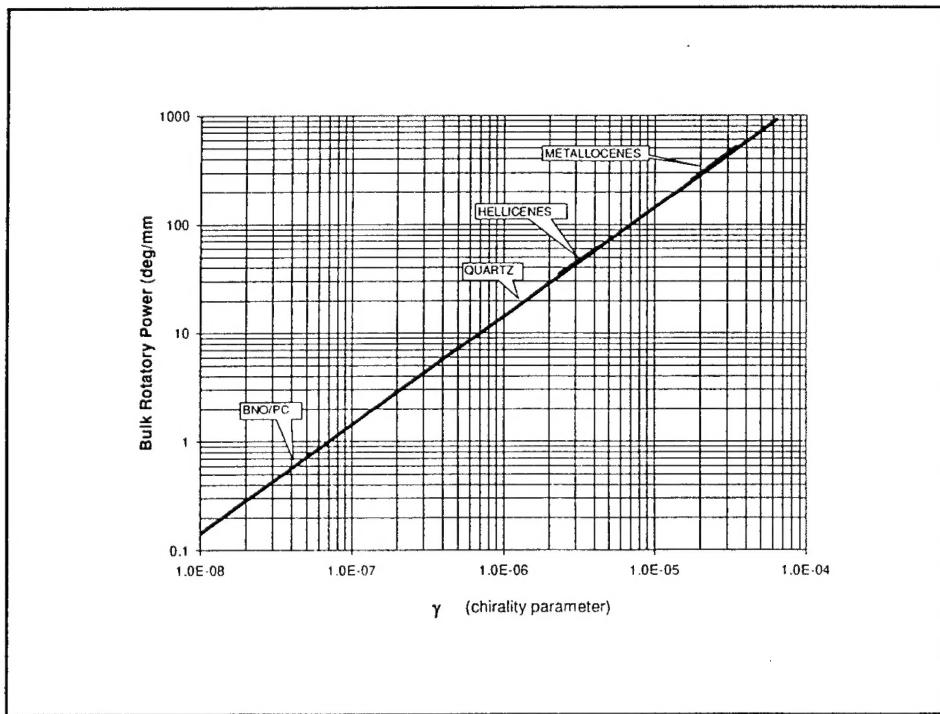
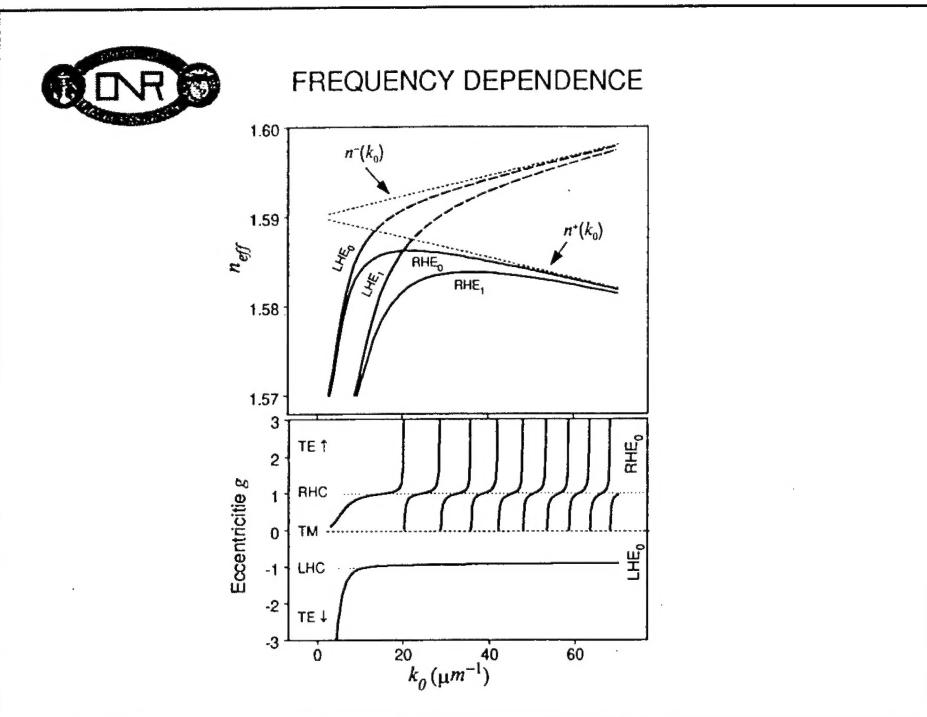
Intersection of RHE₀ with LHE₁

[Transition region where only LH polarization]

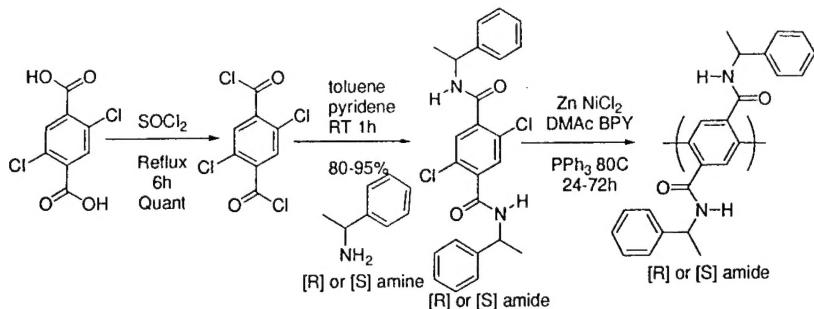


Transition; TE/TM \Rightarrow LHC/RHC





Synthesis of the Chiral Amide Monomer

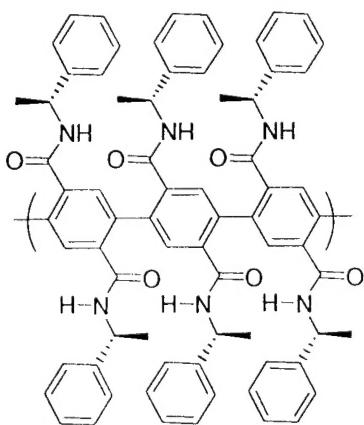


Monomer Preparation [2,5-Dichloro-N,N'-bis-(1-phenyl-ethyl)-terephthalamide]

2,5-dichloro-terephthalic acid (20.0g, 85.1 mmol) was refluxed in thionyl chloride (100 ml). After 6 hours, the thionyl chloride was removed under reduced pressure to yield the product in near quantitative yield and was used without purification.

The acid chloride (5.0 g, 18.4 mmol) was dissolved in dry toluene (50 mL) and triethyl amine (5.1 mL, 2 eq.) and [R] 1-phenyl-ethyl amine (5.0 mL, 2.1 eq, 38.6 mmol) were added. The reaction mixture was stirred overnight and was then filtered to yield the amide in ~95% yield. The resulting solid was recrystallized from acetonitrile three times to afford a polymerization quality monomer.

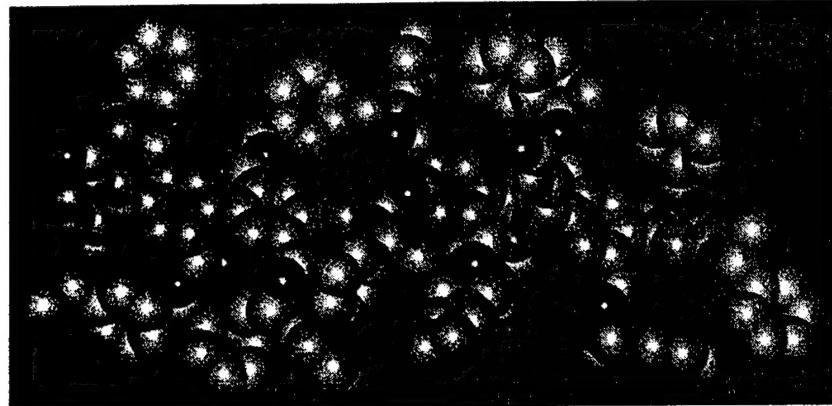
Poly(p-Phenylene) with Chiral Amide Side-chains



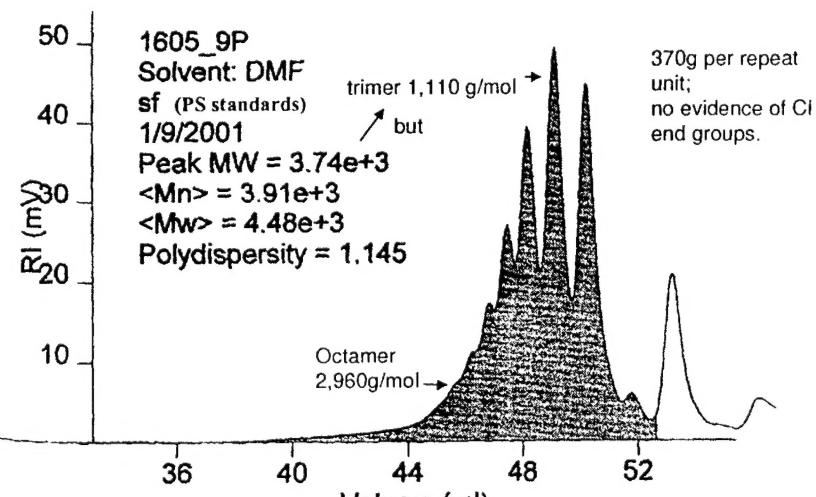
Polymerization Conditions

A suspension of anhydrous NiCl_2 (0.147g, 1.13 mmol), 2,2' bipyridine (0.177g, 1.13 mmol), triphenyl-phosphine (1.89g, 4.53 mmol), and zinc powder (0.370g, 5.66 mmol) in DMAc (50 mL) was heated to 50 C until it has obtained a red color. To that was added the amide monomer (5.000 g, 11.33 mmol). The reaction mixture was heated to 90 C for 24 hrs, then precipitated into 1M HCl. The resulting solid was reprecipitated from acetone into water several times to yield a white polymer (74%).

Poly(p-Phenylene) with Chiral Amide-Side-chains.
The backbone is green, oxygen is red, nitrogen is dark blue, and other carbons are light blue)

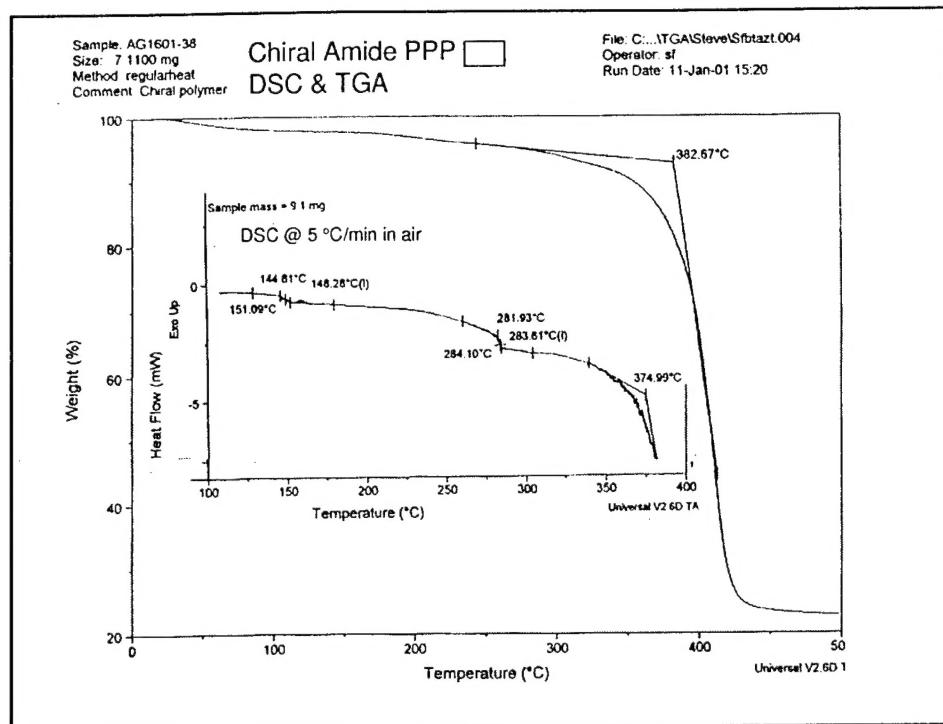


GPC of Chiral Amide-PPP



Sample DI 1605-09

NMP solvent

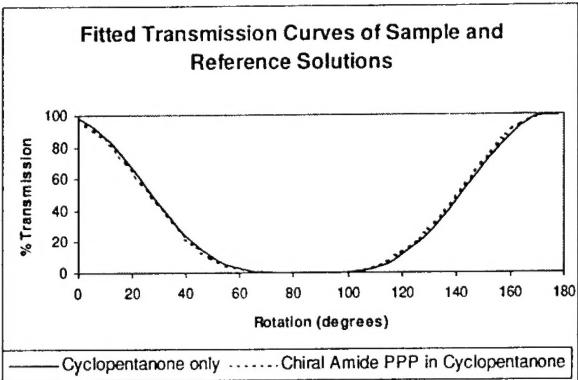


Optical Film Preparation Technique

NMP (N-methyl pyrrolidinone) was used to make the 20 wt % solutions poly(p-phenylene)'s. Films spun from NMP at 2000-3000 rpm were 1-to 2-microns thick (based on reflected light interference patterns), and remained crack-free. The drying program for the films was 70 C under dry nitrogen overnight.

[Note: 20 wt. % polymer solutions in cyclopentanone gave films with cracks at the edge that within two days propagated throughout the film, preventing optical characterization. Its lower boiling may have been the problem.]

Estimating Intrinsic Rotary Power of the Chiral Amide-PPP via Solution Polarimetry



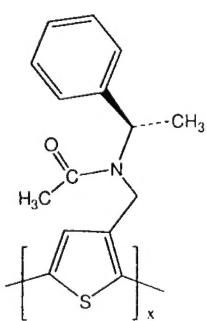
Intrinsic Rotary Power was estimated to be -71° in a UV-Vis spectrometer experiment passing a beam of light at 625 nm through sample solutions between rotating crossed polarizers, and measuring the change in transmission between a sample of pure solvent and a sample of polymer solution.

Solvent: Cyclopentanone
Concentration: 0.18 g / mL

Equation form: $\%T = \cos^4(\text{rotation angle} - \phi)$; where ϕ = phase shift between pure solvent and polymer solution for a 1 cm path length. Note: IRP is per 10 cm path length.
[A positive phase shift is counterclockwise along propagation direction.]

Preparation Of A Chiral Polythiophene

Monomer Synthesis:



5 mL 3-formylthiophene (57 mmoles) and 7.4 mL α -methylbenzylamine (57 mmoles) in 100 mL THF was stirred overnight with 4 Å molecular sieves then filtered. 2.16 grams NaBH₄ was added followed by 100 mL MeOH dropwise. The solution was cooled and concentrated in vaccum. The residue was taken up in 200 mL CH₂Cl₂ and washed with water, dried (MgSO₄) and concentrated in vaccum to give 11.35 grams of a brown liquid (92%). This was chromatographed on Silica Gel using 20% ethyl acetate/hexanes to give 10.65 grams of a clear light yellow liquid (86%). To a solution of 8.34 grams of this thiophene liquid (38 mmoles) in 50 mL chloroform, 4.0 mL acetic anhydride (42 mmoles) were added. The solution was stirred for 48 hours then washed with water, dried (MgSO₄) and concentrated in vaccum to give 10.84 grams of a straw colored liquid (100%). This was chromatographed on Silica Gel using 40% ethyl acetate/hexanes to give 9.44 grams of a clear oil (96%).

Polymer Synthesis: 0.52 grams of monomer (2 mmoles) in 25 mL chloroform was added to 1.30 grams anhydrous ferric chloride (8 mmoles) in portions over 60 minutes. The mix was heated to reflux and stirred overnight, cooled and filtered. The solids were washed with chloroform, suspended in 50 mL hot water, then filtered and washed with hot water to give 0.33 grams of a dark solid.